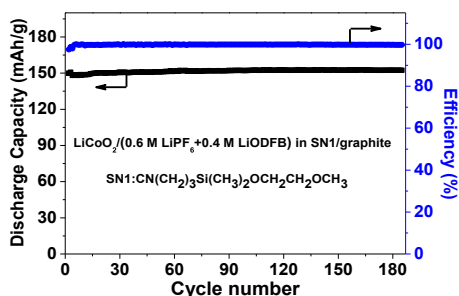Short communication

Organosilicon compounds containing nitrile and oligo(ethylene oxide) substituents as safe electrolytes for high-voltage lithium-ion batteries

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HIGHLIGHTS

- Organosilicon compounds synthesized as safe electrolytes for high-voltage Li-ion batteries.
- First report of organosilicon electrolytes cycled stably at 4.4 V in $LiCoO_2$/graphite cell.
- Delivered a discharge capacity of 152 mAh g^{-1} for 185 cycles with negligible decay at 0.2 C rate.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Organosilicon compounds containing nitrile and oligo(ethylene oxide) substituents are synthesized as safe electrolytes for high-voltage lithium-ion batteries. We firstly report that these organosilicon electrolytes could be stably cycled at an upper cutoff voltage of 4.4 V in $LiCoO_2$/graphite full cells.

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1. Introduction

To address the energy density problem of lithium-ion batteries (LIBs) confronted in the applications for electric vehicles [1–3], many high-voltage cathode materials [4–6], such as lithium rich materials $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$, transition metal-substituted spinel materials ($LiM_xMn_{2-x}O_4$, M = transition metal), and polyanion materials with Ni/Co cations, have been developed for improving the energy and power densities of LIBs. However, the major hurdles preventing these materials from practical applications are the anodic stability limits of the conventional carbonate-based electrolyte solvents on highly oxidative surfaces of these charged cathodes and the safety issues related with these high flammable electrolytes when applied in the high-voltage lithium-ion batteries [1–3].

Recently, ionic liquids [7,8], fluorinated compounds [9,10], sulfone- [11–13], nitrile- [14–17], and organosilicon-based electrolytes [18–21] have been investigated as alternatives to carbonate-based electrolytes for high-voltage application due to their high safety features. Among them, organosilicon electrolytes have attracted a great attention owing to their thermal and electrochemical stability, low flammability, and environmentally benign character [18–21]. Recently, computational [22] and experimental attempts [23,24] have been reported to improve the oxidation

stability of organosilicon compounds. For instance, trimethylsiloxy compound with tri(ethylene oxide)(EO) substituent (1NM3) doped with lithium bis(oxalate)borate (LiBOB) showed good cycling performance at an upper cutoff voltage of 4.2 V in Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$/MAG-graphite cell; but displayed severe capacity fading at 4.3 V with only 50% capacity retention after 10 cycles [23]. We recently reported that triethoxysilyl compound with di(EO) substituent (TESM2) with 1 M LiPF$_6$ exhibited good cycling stability in high-voltage-LiCoO$_2$/Li half cell cycled over 3.0–4.35 V, with 90% capacity retention after 80 cycles [24].

In this communication, we rationally designed and synthesized a series of novel organosilicon compounds containing nitrile group (CN) and EO substituents as electrolyte solvents for high-voltage LIBs, aiming to combine the high safety of organosilicon electrolytes [18–21] and the high oxidative potential feature of nitrile compounds [14–17]. Scheme 1 displays the synthesis of these organosilicon compounds (details see Supporting information) and the chemical structures of the reference compounds for comparison. The synthesized organosilicon compounds as electrolyte solvents with LiPF$_6$ and lithium oxalyldifluoroborate (LiODFB) binary salts showed excellent cycling stability over 2.7–4.4 V in high-voltage-LiCoO$_2$/graphite full cells. So far as we know, this is the first report that organosilicon electrolytes could be stably cycled at an upper cutoff voltage of 4.4 V.

2. Results and discussion

The physical properties for these compounds, such as dielectric constant (ε), viscosity (η), and ionic conductivity (σ) are collected in Table 1. The DSC curves showed only one second-order phase inflection for glass transition (T_g) (Fig. S1), indicating that these compounds are in a completely amorphous state within the low temperature range studied, which would be desirable for low temperature application [25,26]. ε, η, and T_g increased with increasing the EO chain length for SNn or the number of EO arms linked to Si atom for SN1, BNS, and TNS. Due to the introduction of polar CN group, the dielectric constant of SN1 is 3 times larger than its analogue without CN substitution (1NM1); the viscosity of SN1 increased 5.8 times than 1NM1 correspondingly [25,26]. Usually, high dielectric constant facilitates the dissociation of lithium salts, thus improves ionic conductivity; while high viscosity limits the mobility of Li$^+$ and decreases the ionic conductivity. As a consequence, SN1 only showed a similar ionic conductivity with 1NM1 owing to its higher viscosity even though it has a higher dielectric constant. SN3/TNS exhibited much higher ionic conductivity than

1NM3 and its analogue PC–1NM3 containing highly polar cyclic carbonate group (Table 1). Arrhenius plots of the ionic conductivity of these compounds doped with 1 M lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI) were slightly curved (Fig. S2). The $\ln(\sigma T)$ versus $(T - T_0)^{-1}$ plots fitted well linearly (Fig. S3), where T_0 and other parameters were derived from VTF equation [25,26] and listed in Table 1. These results demonstrate that the motion of EO units is involved in the transportation of Li-ions in the electrolyte.

The electrochemical windows of SNn, BNS, and TNS with 1 M LiTFSI were determined by linear sweep voltammetry (Fig. 1a). SNn, BNS, and TNS compounds oxidatively decomposed at around 5.1 V (vs. Li/Li$^+$). Compared with the oxidative limit of 4.4 V for 1NM1 [25,26], the CN substitution might increase the oxidative limit to 5.12 V for SN1. All SNn compounds with one EO arm degraded reductively at around 0 V. Interestingly, the reductive potentials for BNS and TNS with multiple EO arms shifted to a much higher potential of 1.1 V, which makes these compounds possible as film forming additives for anodes [27–29].

Preliminary investigations were performed using these compounds as electrolyte solvents for high-voltage lithium-ion cells. LiCoO$_2$/Li half cell with 1 M LiPF$_6$ in SN1 as an electrolyte delivered a high specific capacity of 165 mAh g^{-1} at 0.2 C (1 C = 170 mA g^{-1}) rate, matching with a high cutoff voltage of 4.4 V (Fig. 1b). But, the voltage profile of Li/graphite cell with 1 M LiPF$_6$ in SN1 showed a long plateau at ~0.43 V instead of the lithium intercalation plateau characterized in a voltage range of 0.20–0.05 V (Fig. 2a), probably resulted from the reductive decomposition of nitrile containing compounds at low potential before the lithium intercalation into graphite [14–16]. However, such incompatibility of 1 M LiPF$_6$–SN1 electrolyte with graphite anode was nicely circumvented by partially replacing LiPF$_6$ with 0.4 M LiODFB which could form solid electrolyte interphase (SEI) films on the surface of graphite (Fig. 2a) [30–32]. As mentioned above, 1 M LiPF$_6$ BNS electrolyte without LiODFB showed good compatibility with graphite even in the presence of 60 vol.% propylene carbonate (PC, a graphite exfoliating solvent [3]). The characteristic plateau of lithium intercalation at ~0.2 V was clearly observed [33,34]. Before this long lithium intercalation plateau, the inclined plateau at 1.0–0.72 V can be attributed to the formation of SEI film originated from the reductive decomposition of BNS (Fig. 2a) [28]. The LiCoO$_2$/graphite full cell using (0.6 M LiPF$_6$ + 0.4 M LiODFB)/SN1 electrolyte delivered a discharge capacity of 152 mAh g^{-1} after 185 cycles and exhibited a negligible capacity decay over a voltage range of 2.7–4.4 V at 0.2 C rate (Fig. 2b). This good cycling stability could also be evidenced by the negligible difference of voltage hysteresis at 1st, 95th and 185th cycle, indicating the excellent electrochemical stability of the electrolyte at the upper cutoff voltage of 4.4 V over cycling (Fig. 3a). As a comparison, the capacity of LiCoO$_2$/graphite cell with the carbonate-based reference electrolyte of 1 M LiPF$_6$–EC/DMC/DEC (1:1:1, by vol.) faded rapidly under the same test conditions (Fig. S4). Moreover, LiCoO$_2$/graphite full cell with SN1 electrolyte also exhibited good rate performance, retaining 90% capacity of 0.2 C at 0.5 C rate (Fig. 3b). When cycled at 0.2 C after 2 C test, the cell fully recovered its capacity to the former 0.2 C level of 152 mAh g^{-1}. BNS and TNS with (0.6 M LiPF$_6$ + 0.4 M LiODFB) also showed comparable cycling performance with SN1 in LiCoO$_2$/graphite full cell (Fig. S5).
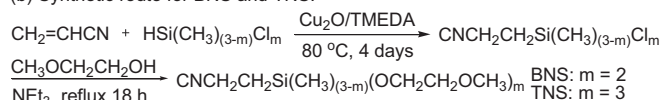
3. Conclusion

In summary, a series of novel organosilicon compounds containing nitrile and EO substituents are designed and synthesized as safe electrolytes for high-voltage lithium-ion batteries. These compounds show high dielectric constants and high oxidative potentials due to the introduction of nitrile and oligo(ethylene oxide)
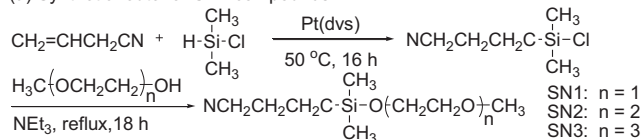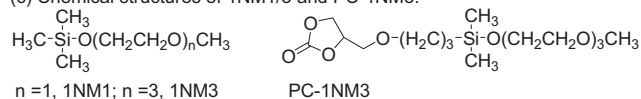

Scheme 1. Synthetic routes of the organosilicon compounds (a, b) and the chemical structures of the reference compounds (c).

Table 1
Physical data, conductivity, VTF parameter and electrochemical window for organosilicon compounds.

Compound	η [cP]	ε	T_g [°C]	σ^a [mS cm^{-1}]	$E_{cathodic}$ [V]	E_{anodic} [V]	EW [V]	T_0 [°C]	E_a [kJ mol^{-1}]	σ_0 [mS cm^{-1}]
SN1	2.88	11.6	−118	1.10	0.0	5.12	5.12	−107.7	5.63	195
SN2	4.62	12.3	−111	1.52	0.0	5.11	5.11	−52.5	2.03	35.0
SN3	7.16	12.8	−98.4	1.20	0.0	5.05	5.05	−128.9	6.64	199
BNS	3.60	15.7	−107	1.28	1.11	5.60	4.49	−74.6	2.66	30.9
TNS	4.60	17.3	−106	1.03	1.09	5.20	4.11	−87.5	3.26	34.4
1NM1[b]	0.50	3.87	−148	1.40	–	4.40	–	−134	3.10	15.0
1NM3[b]	1.40	5.13	−116	1.80	–	4.40	–	−67.2	2.10	27.0
PC−1NM3[c]	262	–	–	0.13	–	–	–	–	–	–

EW: electrochemical window.
[a] Conductivities were measured with 1 M LiTFSI at 25 °C.
[b] Ref. [9].
[c] Ref. [7].
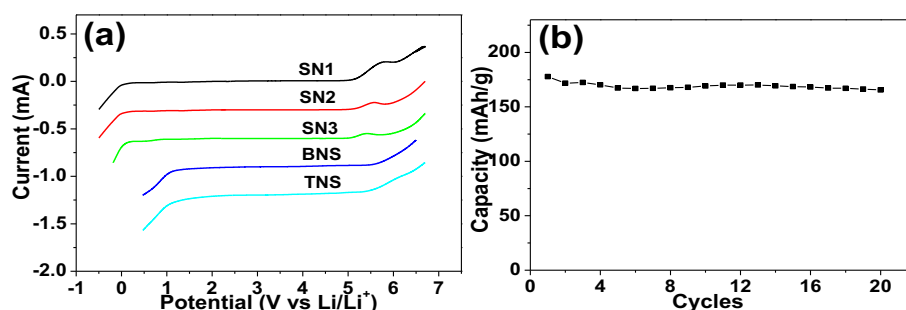
Fig. 1. (a) Linear scanning voltammetry of the synthesized organosilicon compounds; (b) cycling performance of LiCoO$_2$/Li half cell.
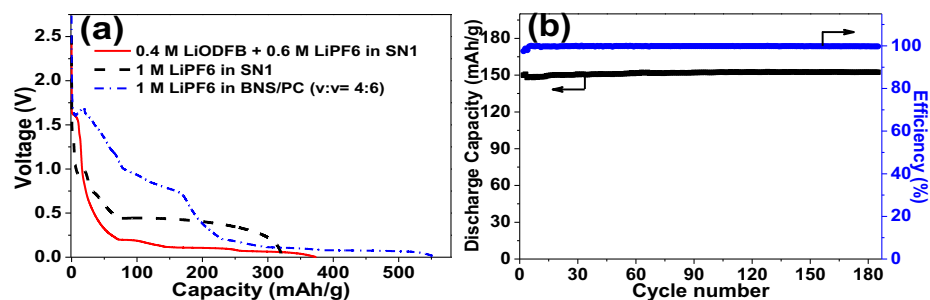
Fig. 2. (a) First voltage profiles of graphite electrodes; (b) cycling performance of LiCoO$_2$/graphite full cell.
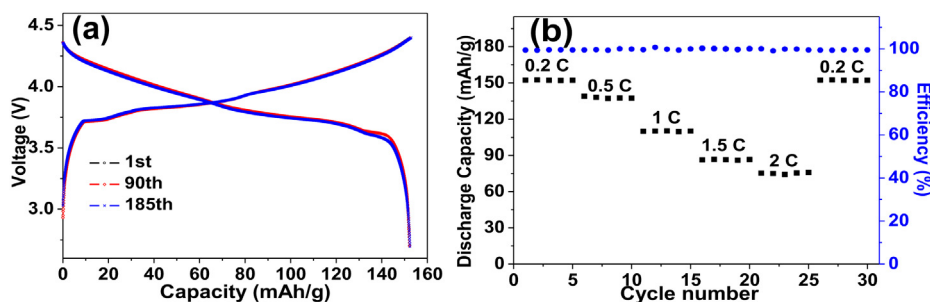
Fig. 3. (a) Charge−discharge profiles; (b) C-rate performance.

substituents. LiCoO$_2$/graphite full cells using them with (0.6 M LiPF$_6$ + 0.4 M LiODFB) binary salts as electrolytes exhibit excellent cycling stability and rate capability at a high cutoff voltage of 4.4 V. The compounds with multiple EO arms (BNS/TNS) show interesting film forming capability on graphite anode. This work demonstrates that these organosilicon compounds have considerable potential as safe electrolytes for the applications in high-voltage lithium-ion batteries.

Acknowledgements

Appendix A. Supplementary information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.12.087.

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